Moderne Composite Flaschen und die Anforderungen für deren sicheren Betrieb aus Sicht der Speicherhersteller

Dynetek Europe GmbH
Dr. C. Rasche

Berlin, 18 Nov. 2003
Various Designs of Composite Cylinders

**Fibres:**
- Glass
- Aramid
- Carbon

**Matrix Materials:**
- Polyester
- Epoxy
- Nylon

**Liner:**
- Al (6061 T6)
- Al (6069)
- Al (70XX)
- 34CrMo4
- Stainless Steel
- Nylon
- Polyethylene

**Hoop wrapped**

**Fully wrapped**
Comparison of the properties of various fibre materials with metal alloys

- **Density, g/cm³**
  - Steel
  - Aramid fibres
  - Glass fibres
  - Ti
  - Al

- **Tensile strength, MPa**
  - Carbon fibres
  - HST
  - IM
  - HM

- **Modulus of elasticity, G Pa**
  - 0
  - 200
  - 400
  - 600

**ADVANCED LIGHTWEIGHT FUEL STORAGE SYSTEMS™**
<table>
<thead>
<tr>
<th>Performance:</th>
<th>Glass Fibres</th>
<th>Aramid Fibres</th>
<th>Carbon Fibres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific strength*</td>
<td>▼</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Impact</td>
<td>▼</td>
<td>↑</td>
<td>▼</td>
</tr>
<tr>
<td>Fatigue</td>
<td>▼</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Creep</td>
<td>▼</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Effects of moisture, acids, bases</td>
<td>▼▼</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>UV radiation</td>
<td>↑</td>
<td>▼</td>
<td>↑</td>
</tr>
<tr>
<td>Fire</td>
<td>▼</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Costs</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>
Environmental Attack and Mechanical Stress on a Composite Vessel on a Natural Gas Powered Vehicle

- Valve connection
- Antifreeze
- Oil and additives
- Water
- Petrol/diesel
- Salts
- Detergents
- Stone impingement
- Creep Strength

Operating pressure 200/300 bar

- CH₄
- CO₂
- O₂
- H₂S
- H₂O
- Oil
- Pentane
- Pentane Ethene
- N₂
- Steam
- Hoop wrap
- Helical winding
- Global radiation
- Cycle Life
- Safety equipment
- Surface Quality

ADVANCED LIGHTWEIGHT FUEL STORAGE SYSTEMS™
Demonstrated track record of effective certification process management

International Certification

ISO 11439
INTERNATIONAL

ECE R 110
EUROPE

NGV 2
UNITED STATES / JAPAN / MEXICO / ARGENTINA

KHK
JAPAN

FMVSS 304
UNITED STATES

TÜV
GERMANY

NFPA 52
NATIONAL FIRE PROTECTION ASSOCIATION

DRIRE
FRANCE

CSA B51
CANADA / AUSTRALIA / HUNGARY / UNITED KINGDOM

Bureau Veritas
ARGENTINA

ADVANCED LIGHTWEIGHT FUEL STORAGE SYSTEMS ™
Raw Material Tests
Mechanical Integrity: Burst Tests, Fatigue Tests
Bonfire
Impact: Bullet-/ Drop Test
Environment: Battery Acid, High-/ Low Temperatures/ Humidity
CNG Type IV: Leak, Permeation, Natural Gas Cycling
Boss Torque, Coating
Cross section of a hoop wrapped steel liner

CrMo-Steel
(165 l; 100 kg; Burst at 280 bar)

+ Carbon Fiber Reinforced Epoxy
(+ 9.5 kg; Burst at 580 bar)

35% Weight Reduction
Al Alloy 6061 T6
(174 l; 29 kg; Burst at 100 bar)

+ Carbon Fiber Reinforced Epoxy
(+ 9.5 kg; Burst at 580 bar)

70 % Weight Reduction
Comparison of weights of different CNG storage units

<table>
<thead>
<tr>
<th>V&lt;sub&gt;gas&lt;/sub&gt; [Nm³]</th>
<th>m [kg]</th>
<th>V&lt;sub&gt;cyl&lt;/sub&gt; [l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 bar / 15°C</td>
<td>ρ = 0.835 kg / Nm³</td>
<td></td>
</tr>
<tr>
<td>CNG:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 2</td>
<td>5 x 165</td>
<td>7 x 185</td>
</tr>
<tr>
<td></td>
<td>+ 2 x 115</td>
<td></td>
</tr>
<tr>
<td>Type 3</td>
<td>6 x 185</td>
<td>7 x 185</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8 x 185</td>
</tr>
</tbody>
</table>

- 500 kg - 1200 kg
Superior Vehicle Performance

Extended vehicle driving range
- or less weight
- up to 8 seats more available
- less maintenance & repair
- 30% less wear on the front axle
- 0.5 - 1 kg less gas consumption

Improved Driving Behaviour
# Known In-Service Failures of NGV Cylinders (Since 1976)

- Last update July 2003 -

<table>
<thead>
<tr>
<th>Date</th>
<th>Place of Failure</th>
<th>No. of Failures</th>
<th>Cylinder Manufact.</th>
<th>Cylinder Design</th>
<th>Source of Data</th>
<th>Cause of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2003</td>
<td>Brescia, Italy</td>
<td>one</td>
<td>Faber</td>
<td>Steel liner + glass hoop-wrap</td>
<td>Faber</td>
<td>?</td>
</tr>
<tr>
<td>May 2003</td>
<td>Saarbrucken, Germany</td>
<td>one</td>
<td>Dynetek</td>
<td>Aluminum liner + carbon full-wrap</td>
<td>Dynetek</td>
<td>Bus fire, Emer PRD did not activate</td>
</tr>
<tr>
<td>Sept 2002</td>
<td>Madison, WI USA</td>
<td>one</td>
<td>Pressed Steel</td>
<td>Steel liner + glass hoop-wrap</td>
<td>Ford, Pressed</td>
<td>Vehicle fire, Superior involve PRD did not activate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Steel Tank</td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 2001</td>
<td>Rio de Janiero, Brazil</td>
<td>one</td>
<td>MAT</td>
<td>Steel</td>
<td>Cilbras</td>
<td>Vehicle fire, EMER PRD did not activate</td>
</tr>
<tr>
<td>April 2001</td>
<td>Malaysia</td>
<td>one</td>
<td>Faber</td>
<td>Steel</td>
<td>Petronas</td>
<td>Vehicle arson fire, EMER PRD did not activate</td>
</tr>
<tr>
<td>April 2001</td>
<td>Vitoria, Brazil</td>
<td>one</td>
<td>Cilbras</td>
<td>Steel</td>
<td>Cilbras</td>
<td>Vehicle fire, MAT PRD did not activate</td>
</tr>
<tr>
<td>March 2001</td>
<td>Salvador, Brazil</td>
<td>one</td>
<td>Cilbras</td>
<td>Steel</td>
<td>Cilbras</td>
<td>Vehicle fire, MAT or Thermadyne PRD did not activate</td>
</tr>
<tr>
<td>March 2001</td>
<td>Recife, Brazil</td>
<td>one</td>
<td>Cilbras</td>
<td>Steel</td>
<td>Cilbras</td>
<td>Vehicle fire, OYRSA PRD did not activate</td>
</tr>
<tr>
<td>2000 Dec</td>
<td>Indiana (Nipsco)</td>
<td>one</td>
<td>Norris/PST</td>
<td>Steel</td>
<td>NGV Coalition</td>
<td>Overfill of 2,400 psi cylinder</td>
</tr>
<tr>
<td>1997 to 2000</td>
<td>Venezuela, Argentina, Egypt</td>
<td>multiple</td>
<td>Mat Incendio, Argentoil, Faber</td>
<td>Steel (tube stock with end spun closed)</td>
<td>Enargas, Faber</td>
<td>Pinhole leaks caused by improper end closures</td>
</tr>
</tbody>
</table>
Improvements

- PRD’s and Burst Discs
- System Setup in the vehicle
- Use of Glass Fibers
- Leakage Potential of CNG Type IV
- Retest Methods and Periods
- Quality of the Gas ex Dispenser
- Use of Solenoid Valves
Safety & Testing

- The DyneCell demonstrated superior performance results in the fire test compared to other lightweight cylinders.

- Cylinders were exposed to extreme temperatures from fire for up to 20 minutes without rupturing.
DyneCell Bonfire Test Results

200 bar / 320 l CNG cylinder (W320NGH200G5N, s/n H 4325)
Ceodeux solenoid valve C350 + VTI PRD plug
Shut off valve with innovative PRD
Accident with a steel tank - PRD was not activated
Durchschlagloch
Gasflasche
Brescia Trasporti istituisce una commissione, in accordo con sindacati e case costruttrici

Scoppio sul bus, l’ora delle perizie

Si cerca di individuare la causa dell’incidente di domenica in via Colombo
CNG Type IV Cylinder / Fully wrapped PE-liner (185 l)

(Two openings)

<table>
<thead>
<tr>
<th>Time [Sec]</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pressure [bar]

TH-EL 1
TH-EL 2
TH-EL 3
TH-EL 4
TH-EL 5

Liner material
Polyethylen
Metallic boss
Stainless steel
or Al Alloy 6061

Hoop wrap
Helical winding
Carbon fiber reinforced epoxy

ADVANCED LIGHTWEIGHT FUEL STORAGE SYSTEMS™
CNG Type IV Cylinder Mounted on roof of Pittsburgh transit Bus

- Filled with 200 bar, Bus struck overpass with sufficient force to buckle roof of Bus
- One cylinder punctured and vented
- Other 3 gouged in dome ends
Partners of the EIHP2 Consortium:

Work Packages:

- **WP1**: Overall Coordination
- **WP2**: Refuelling Station
- **WP3**: Refuelling Interface
- **WP4**: Vehicles
- **WP5**: Safety
- **WP6**: Links “EU-USA”, Cluster Activities
UNECE Platform for Globally Harmonized Regulation for H₂ Vehicles

- In Europe, vehicles receive Whole Vehicle Type Approval on the basis of a regulation (legal requirement) and not on the basis of standards.
- In the EU every member state has different regulations and standards concerning H₂ - need for EU-wide harmonization is necessary.
- UNECE WP29 was identified by EIHP1 as platform for EU-wide harmonization with the possibility for later global harmonization of regulations as it is the recognized World Forum.
- EIHP1 developed proposals for draft regulations for CGH₂ and LH₂ road vehicles.
- UNECE suggested to develop Global Technical Regulation (GTR) as a priority and in parallel continue to develop UNECE draft regulations in order to bring vehicles on European roads in time.

ECE Regulation expected by 2005
Global Technical Regulation thereafter

Global approval of H₂ road vehicles
Valve Concept

Frame Rail (DC)

Free space

possibly additional free space

Front view

possibly additional free space

20-30 mm
Today, in fuel cell cars a stored hydrogen mass of 4 kg is considered to be sufficient for a driving range of 640 km (400 miles). This range fulfills the requirements of several OEM’s to support the commercialisation of fuel cell vehicles.
Projects:

- 500 bar cylinder for stationary storage of hydrogen (PED) at filling stations (02/2004)
- hoop wrapped 200 bar and 300 bar cylinder for transport of gas (TPED); fully and hoop wrapped (12/2004)
- 700 bar compressed hydrogen cylinder for vehicles (“EIHP”); funded by the German state Nordrhein-Westfalen (12/2004)
- exchangeable small hydrogen cylinders for portable FCs;
- “cool” filling; recycling
Goal:
- Development, Testing and Design Approval for an entire 700 bar Hydrogen System

Solution Approach:
- UHP Storage Tank based on a fully wrapped Stainless Steel liner
- common SS grade
- Improved Mechanical Properties of the Liner due to Flowforming or Cryoforming by factor 4 (Rp1.0 >800 MPa)
- improved fatigue resistance, suitable for hydrogen
- very flexible liner dimensions

- sponsored by the German State of Northrhine-Westfalia
The Cryoforming Process:

Controlled plastic deformation of a pre-form by internal pressurization with liquid nitrogen.

Result:
Light weight high pressure vessel made of corrosion resistant stainless steel
**First Prototype Vessel**

**SS - Liner made of 1.4541, Weight 16 kg**

<table>
<thead>
<tr>
<th></th>
<th>As received (annealed)</th>
<th>Cryoformed (430 bar/-196°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>189 mm</td>
<td>210 mm</td>
</tr>
<tr>
<td>Wall Thickness</td>
<td>3.8 mm</td>
<td>3.5 mm</td>
</tr>
<tr>
<td>1.0%-Yield Strength</td>
<td>Min. 250 MPa</td>
<td>Min. 950 MPa</td>
</tr>
</tbody>
</table>

**Next Steps:**
- Wrapping
- Autofrettage
- Burst Tests
- Comparison with Design Calculations

**Result:**
Vessel with
- ≈ 21 L Capacity (= 0.84 kg H2)
- ≈ 28 kg Weight
Concept of Cryoforming Metastable Stainless Steels

Stress-Strain curve of AISI 304 at RT and –196°C

- significant strengthening at cryogenic temperatures due to martensitic transformation
- remaining high level of ductility
- degree of strength hardening is controlled by alloy composition
Phase 2: Prototype liner manufacturing

Stainless Steel Liners for lightweight cylinders

Procedure: Manufacture and test liners

<table>
<thead>
<tr>
<th>Prototypes</th>
<th>Stainless Steel Liner for fully wrapped 700 bar Hydrogen Cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>type 1</td>
</tr>
<tr>
<td>production method</td>
<td>welded from flow formed components</td>
</tr>
<tr>
<td>outer liner diameter</td>
<td>Ø 254 mm</td>
</tr>
<tr>
<td>liner wall thickness</td>
<td>approx. 2 mm</td>
</tr>
</tbody>
</table>

Liner burst test

Internal Dynetek requirement

<table>
<thead>
<tr>
<th>Results</th>
<th>215 bar</th>
<th>270 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>245 bar ✓</td>
<td></td>
<td>305 bar ✓</td>
</tr>
</tbody>
</table>
Phase 2: Prototype cylinder manufacturing

Filament winding of stainless steel liners

<table>
<thead>
<tr>
<th>Prototype Data</th>
<th>Type 1 (flow formed)</th>
<th>Type 2 (cryoformed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liner weight</td>
<td>14 kg</td>
<td>13 kg</td>
</tr>
<tr>
<td>Cylinder weight</td>
<td>33 kg</td>
<td>31 kg</td>
</tr>
<tr>
<td>Diameter</td>
<td>300 mm</td>
<td>287 mm</td>
</tr>
<tr>
<td>Water capacity</td>
<td>32 L</td>
<td>30 L</td>
</tr>
</tbody>
</table>
Present Worldwide H₂ FCV & ICEV Developments

- GM/Opel
- PSA
- Nissan
- DaimlerChrysler
- Toyota
- DaimlerChrysler
- Irisbus
- MAN
- Toyota-Hino
- DaimlerChrysler
- Volkswagen/PSI
- Hyundai
- Honda
- Ford
- HaWa - Hamburg

Propulsion with PEM Fuel Cell Electric Powertrains

Propulsion with Internal Combustion Engine Powertrains
Hydrogen Fuel Cell Vehicles on the Road

CUTE Project
27 Fuel Cell Buses for 9 European Cities

- Using 9 of our advanced lightweight DyneCell fuel storage cylinders with 205 l @ 350 bar (app. 47 kg stored hydrogen)
- Expected launch date by the year 2003/2004
Hydrogen Fuel Cell Vehicles on the Road

Hydrogen Fuel Cell Bus
Powered by Siemens’ PEM Fuel Cell

Cylinders: DyneCell V170 x 9
Volume w.c.: 1,548 L
Total Cylinder Weight: 558 kg
Service Pressure: 3600psi/ 250bar
Hydrogen Fuel Cell Vehicles on the Road

Ballard Power Systems
Vancouver – Chicago

Cylinders: DyneCell W316 x 8
DyneCell W210 x 1

Volume w.c.: 2,738 L
Total Cylinder Weight: 809 kg
Service Pressure: 3600psi / 250bar
Hydrogen Fuel Cell Vehicles on the Road

XCELLSiS The Fuel Cell Engine Company

ZEbus (Zero-Emission bus)

Phase 4 Fuel Cell Engine Bus

SunLine Transit, USA

- One of the first out of 25 fuel cell buses to participate in the California Fuel Cell Partnership Program
**Hydrogen Fuel Cell Vehicles on the Road**

**Hydrogen Storage System**
For Munich Airport Buses

<table>
<thead>
<tr>
<th>System No:</th>
<th>0360</th>
<th>0390</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Service Pressure (psi):</td>
<td>3600</td>
<td>3600</td>
<td>3600</td>
</tr>
<tr>
<td>(bar)</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Number of Cylinders:</td>
<td>6</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Storage Volume (ltr):</td>
<td>1032</td>
<td>1548</td>
<td>2580</td>
</tr>
<tr>
<td>Total Cylinder Weight: (kg):</td>
<td>384</td>
<td>576</td>
<td>960</td>
</tr>
<tr>
<td>Dimensions:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length (mm):</td>
<td>2715</td>
<td>3945</td>
<td>6660</td>
</tr>
<tr>
<td>Width (mm):</td>
<td>2160</td>
<td>2160</td>
<td>2160</td>
</tr>
<tr>
<td>Height (mm):</td>
<td>440</td>
<td>440</td>
<td>440</td>
</tr>
</tbody>
</table>

*MAN Technologie*
*Munich, Germany*

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**ADVANCED LIGHTWEIGHT FUEL STORAGE SYSTEMS™**
Nissan introduced this concept fuel cell vehicle at the California Fuel Cell Partnership Program that is equipped with Dynetek’s fuel storage systems.

Nissan Fuel Cell Vehicle (FCV) ‘XTERRA’
FORD P2000
Direct Hydrogen Fuel Cell (HFC) Vehicle

- Same performance as a Ford Taurus
- Using two of our advanced lightweight DyneCell fuel storage cylinders.
- Commercially available by the year 2004, this expected launch date also includes other automobile manufacturers with FCVs.
Hydrogen Fuel Cell Vehicles on the Road

- Unveiled at the California Fuel Cell Partnership’s Grand Opening
- Ford entered into a multi-year Purchase and Supply Agreement with Dynetek
**500 bar Pressure Vessel for Hydrogen**  
( preliminary product description)

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Application:</strong></td>
<td>stationary storage</td>
</tr>
<tr>
<td><strong>Certification:</strong></td>
<td>PED (CE-marking)</td>
</tr>
<tr>
<td><strong>Design:</strong></td>
<td>Steel liner hoop wrapped with carbon fibre</td>
</tr>
<tr>
<td></td>
<td>reinforced epoxy resin (CFRP)</td>
</tr>
<tr>
<td><strong>Type:</strong></td>
<td>CN085PED500H5</td>
</tr>
<tr>
<td><strong>Volume:</strong></td>
<td>85.5 l (± 2.5 l)</td>
</tr>
<tr>
<td><strong>Dimensions:</strong></td>
<td>D = 285.4 mm (± 1%)</td>
</tr>
<tr>
<td></td>
<td>L = 1950 mm (± 20 mm)</td>
</tr>
<tr>
<td><strong>Weight:</strong></td>
<td>157 kg (-6% / +12%)</td>
</tr>
<tr>
<td><strong>Working Pressure:</strong></td>
<td>500 bar / 15°C (p(_{\text{max}}) = 56.4 Pma @ 50°C)</td>
</tr>
<tr>
<td><strong>Test Pressure:</strong></td>
<td>75 MPa</td>
</tr>
<tr>
<td><strong>Service Temperature:</strong></td>
<td>-40°C up to 50°C</td>
</tr>
<tr>
<td><strong>Thread:</strong></td>
<td>Dual Port 1.125&quot;-12 UNF (with O-Ring)</td>
</tr>
<tr>
<td><strong>Surface:</strong></td>
<td>Steel with powder coating RAL3000 (red); CFK natural</td>
</tr>
<tr>
<td><strong>Price (appr.):</strong></td>
<td>1026 € / piece</td>
</tr>
<tr>
<td><strong>Availability:</strong></td>
<td>probably end of 2003 / beginning of 2004</td>
</tr>
</tbody>
</table>